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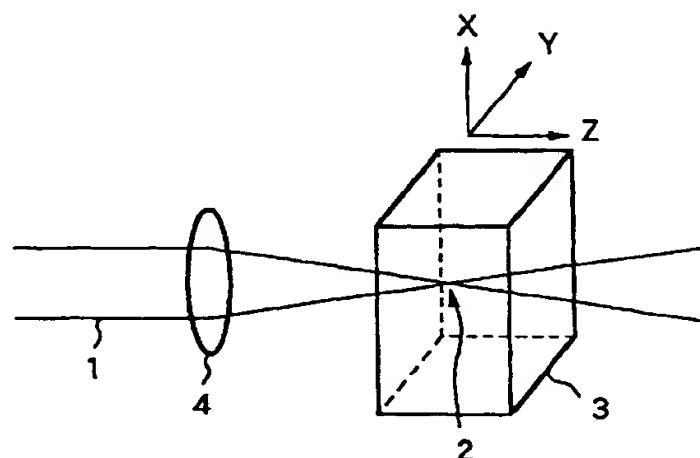
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## (54) METHOD OF SELECTIVELY CHEMICALLY CHANGING INSIDE OF INORGANIC MATERIAL AND INORGANIC MATERIAL INSIDE OF WHICH IS SELECTIVELY CHEMICALLY CHANGED

(57) An inorganic body 3 containing rare earth and/or transition metal ion is irradiated with a pulsed laser beam 1, in the manner such that a focal point 2 of the pulsed laser beam 1 is adjusted to an inner part of the inorganic body 3. The inorganic body 3 may be a glass or crystal containing one or more of oxide, halide and chalcogenide. The rare earth ion may be one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm, Tb. The transition metal ion may be one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru. When the focal point 2 is relatively shifted with respect to the inorganic body 3, an ionic valence-changed domain is formed with a predetermined pattern at the inner part of the inorganic body 3. The pulsed laser beam is preferably with pulse width under a picosecond. The ionic valence change occurs at the focal point 2 and its vicinity but the rare earth or transition metal ion keeps its original valence at the other part, so as to form a reformed domain with a predetermined pattern in the inorganic body 3. Since optical properties are selectively changed at the reformed domain, the processed inorganic body 3 is useful as a functional device such as a memory device or a light-emitting device using the differentiated optical properties.

FIG.1



**Description****TECHNICAL FIELD OF THE INVENTION**

**[0001]** The present invention relates to a method of selectively reforming an inner part of an inorganic body by irradiation with a condensed pulsed laser beam and a new inorganic body produced thereby.

**BACKGROUND OF THE INVENTION**

**[0002]** When an inorganic body containing rare earth or transition metal ion is subjected to oxidization-reduction or irradiated with an X-ray or ultraviolet beam, a valence of the rare earth or transition metal ion changes. For instance, J. Qiu et al. reported change of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  by irradiating  $\text{Eu}^{2+}$ -containing fluoride with an X-ray or ultraviolet beam, in Appl. Phys. Lett. 71 (1997) 759. W. A. Weyl reported change of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  by irradiating  $\text{Mn}^{2+}$ -containing oxide with an ultraviolet beam, in Coloured Glasses, Society of Glass Technology (1951).

**[0003]** In order to realize valence change of rare earth or transition metal ion at a specified part of an inorganic body, the inorganic body is covered with a shading mask having a predetermined pattern, and then selectively irradiated with an X-ray or ultraviolet beam. The valence of the ion is partially changed at a part defined by the pattern of the shading mask.

**[0004]** Valence of rare earth or transition metal ion can be also changed by an oxidization-reduction method in a controlled atmosphere. In this case, valence change occurs over a whole of the inorganic body, but it is difficult to selectively change a part of the ion in the inorganic body. On the other hand, valence change of ion induced by irradiation with a X-ray or ultraviolet beam depends on a reaction in one photon process, so that an energy of the X-ray or ultraviolet beam is absorbed in a surface layer of the inorganic body. As a result it is difficult to selectively change valence of the ion only at an inner part of the inorganic body.

**[0005]** Conventional methods have difficulty for selectively changing ion valence at a specified inner part of an inorganic body, as above-mentioned.

**SUMMARY OF THE INVENTION**

**[0006]** The present invention is accomplished to overcome such the problems as above-mentioned. The present invention aims at provision of a new inorganic body improved in functionality by selective valence change of rare earth or transition metal ion at its specified inner part. The selective valence change is realized by irradiating an inorganic body containing rare earth and/or transition metal ion with a condensed pulsed laser beam of wavelength different from absorption wavelength of the rare earth and/or transition metal ion.

**[0007]** According to the present invention, a pulsed laser beam of wavelength different from absorption wavelength of rare earth and/or transition metal ion emitted to an inorganic body containing rare earth and/or transition metal ion in the manner such that a focal point of the pulsed laser beam is adjusted to an inner part of the inorganic body. Such the condensing irradiation induces valence change of the rare earth and/or transition metal ion only at the focal point and its vicinity.

**[0008]** The inorganic body may be a glass or crystal containing one or more of oxides, halides and chalcogenides. Rare earth ion may be one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm and Tb ions. Transition metal ion may be one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.

**[0009]** When the focal point is relatively shifted with respect to the inorganic body, a domain with a predetermined pattern where the rare earth and/or transition metal ion changes its valence is formed at an inner part of the inorganic body. The pulsed laser beam is with pulse width under a picosecond.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0010]**

Fig. 1 is a schematic view for illustrating an inorganic body irradiated with a pulsed laser beam which is condensed at a focal point adjusted to an interior of the inorganic body.

Fig. 2 is a schematic view for illustrating a confocal optical system useful for measuring an ionic valence-changed domain.

Fig. 3 is a graph which indicates valence change of rare earth or transition metal ion by condensing irradiation with a pulsed laser beam.

**PREFERRED EMBODIMENT OF THE PRESENT INVENTION**

**[0011]** A pulsed laser beam useful in the present invention is of wavelength which does not overlap characteristic absorption wavelength of an objective inorganic body including absorption wavelength of rare earth or transition metal ion. As far as a pulse energy of 50% or more on the basis of a total irradiation energy is obtained, ionic valence change occurs only at a focal point.

**[0012]** A pulsed laser beam is with pulse width under a picosecond. Since a peak power of the pulsed laser beam becomes smaller as elongation of the pulse duration, a peak energy of the pulsed laser beam shall be greater in order to obtain a similar peak power density. The peak power of the pulsed laser beam is represented by a power (W) which is a divided value of an energy (J) per 1 pulse by pulse width (sec), and the peak power density is represented by a ratio ( $\text{W}/\text{cm}^2$ ) of

the peak power (W) to a unit area ( $\text{cm}^2$ ).

[0013] Pulse width is preferably controlled within a range of 100-500 femtoseconds. If an inorganic body is irradiated with a laser beam with pulse width narrower than 100 femtoseconds, pulse width in an inner part of the inorganic body is greatly varied in response to a position of a focal point along a direction of depth, since the inorganic body itself is a dispersion material. Consequently, it is difficult to dimensionally control a domain where ionic valence change occurs. If the pulse width is over 500 femtoseconds on the contrary, the inorganic body is likely damaged when its inner part is irradiated with a condensed pulsed laser beam with a peak energy sufficient for ionic valence change.

[0014] A pulsed laser beam 1 is condensed by a condenser lens 4 so as to position a focal point 2 at an inner part of an inorganic body 3, and emitted to the inorganic body 3, as shown in Fig. 1. When an electric field intensity of the pulsed laser beam 1 at the focal point 2 exceeds a certain threshold in response to valence change of rare earth or transition metal ion, the rare earth or transition metal ion changes its valency at the focal point 2 and its vicinity. A position apart from the focal point 2 is subjected to an electric field of intensity insufficient for occurrence of ionic valence change. As a result, the valence change of the rare earth or transition metal ion occurs only at the focal point 2 and its vicinity, and the inner part of the inorganic body 3 is selectively reformed.

[0015] A domain where such ionic valence change occurs can be shaped to a predetermined pattern by relative movement of the focal point 2 with respect to the inorganic body 3. For instance, the ionic valence-changed domain is shaped to a two- or three-dimensional pattern by shifting the focal point 2 along directions of X, Y, Z by operation of an optical system, siting the inorganic body 3 along directions of X, Y and Z, or shifting both the focal point 2 and the inorganic body 3.

[0016] The inner part (reformed part) of the inorganic body 3 at the focal point 2 and its vicinity is the ionic valence-changed domain, while rare earth or transition metal ion at the remaining part (unreformed part) is still of its original valence. The resulting differentiated ionic valence between the reformed and unreformed parts causes differences in optical characteristics such as light absorption and light emission. The inorganic body reformed in this way is useful as a functional device such as an optical memory device, light-emitting device or amplifier device, using such the differentiated ionic valence.

[0017] The present invention will be more apparent from the following examples. Of course, these examples do not put any restrictions on the scope of the present invention.

#### EXAMPLE 1

[0018]  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Eu}_2\text{O}_3$  raw materials were

weighed and mixed together to prepare oxide glass composition which contained cations at ratios of 73mol%  $\text{Si}^{4+}$ , 25mol%  $\text{Na}^+$  and 2mol%  $\text{Eu}^{2+}$ . The mixture was put in a Pt crucible and melted 30 minutes at 1450°C and then cooled to a room temperature. A glass obtained in this way was received in a carbon crucible and subjected 60 minutes to a reducing reaction at 1450°C in an atmosphere of 5vol.%  $\text{H}_2\text{-N}_2$ . Thereafter, the glass melt was rapidly cooled together with the crucible to a room temperature, to obtain a  $\text{Eu}^{2+}$ -containing oxide glass.

[0019] A testpiece of 5mm in thickness was cut off the  $\text{Eu}^{2+}$ -containing oxide glass. Two planes of the testpiece were polished at an optical level and examined by spectral analysis for measuring absorption spectrum. Presence of  $\text{Eu}^{2+}$  in the oxide glass was detected by the spectral analysis.

[0020] The testpiece was then irradiated with a pulsed laser beam 1 which was condensed by a condenser lens 4 in a manner such that a focal point 2 is positioned at an inner part of the testpiece 3, as shown in Fig. 1. The pulsed laser beam was of 800nm wavelength with 300 femtoseconds pulse width and 1kHz a repetition rate oscillated from a Ti-sapphire laser excited with an argon laser.

[0021] A light beam of 400nm wavelength was emitted to and condensed at the same focal point 3 of the testpiece after being irradiated with the condensed pulsed laser beam, using a confocal optical system (shown in Fig. 2). In this confocal optical system, a laser beam 1 which held diffraction minimum penetrates a tube lens 5 and an objective lens 6, and condensed in a surface or inner part of the testpiece 3. When a condensing plane 7 is adjusted to the inner part of the testpiece 3, a light through the condensing plane 7 penetrates the objective lens 6 and tube lens 5, and is imaged on a confocal pin-hole 9 by a beam splitters 8. Since light beams emitted from the other parts except the condensing plane 7 of the testpiece 3 are effectively separated by the confocal pin-hole 9, characteristic changes, i.e. ionic valence change, at the focal point 3 is proven from a fluorescence spectrum obtained by detecting the image formation with a photodetector 10.

[0022] Fig. 3 is a measuring result of a fluorescence spectrum (a) from a part corresponding to the focal point 2 (shown in Fig. 1). Presence of a fluorescence spectrum originated in  $\text{Eu}^{3+}$  is noted in Fig. 3. For comparison, a fluorescence spectrum from the other part except the focal point 2 was measured in the same way.

In this case, a fluorescence spectrum (b) originated in  $\text{Eu}^{2+}$  was detected. It is apparently recognized by comparing these fluorescence spectra (a) and (b) that valence of Eu ion was changed from 2+ to 3+ at the focal point 2 and its vicinity by emitting the pulsed laser beam 1 to and condensing it at the inner part of the testpiece 3. The same valence change of Eu ion from 2+ to 3+ were detected by emitting a pulsed laser beam and condensing it at an inner part of another glass contain-

ing halide, sulfide or chalcogenide in the same way.

## EXAMPLE 2

**[0023]** AlF<sub>2</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>, YF<sub>3</sub>, SmF<sub>2</sub> raw materials were weighed and mixed together to prepare fluoride glass composition which contained cations at ratios of 35mol% Al<sup>3+</sup>, 10mol% Mg<sup>2+</sup>, 20mol% Ca<sup>2+</sup>, 10mol% Sr<sup>2+</sup>, 10mol% Ba<sup>2+</sup>, 14mol% Y<sup>3+</sup>, and 1mol% Sm<sup>2+</sup>, and an anion sole of F<sup>-</sup>. The mixture was put in a carbon crucible and reductively melted 60 minutes at 1000°C in an atmosphere of 5 vol.% H<sub>2</sub>-N<sub>2</sub>. Thereafter, the glass melt was rapidly cooled together with the crucible to a room temperature.

**[0024]** A testpiece was cut off an obtained Sm<sup>2+</sup>-containing fluoride glass. Two planes of the testpiece were polished at an optical level and examined by spectral analysis for measuring absorption spectrum. Presence of Sm<sup>2+</sup> in the oxide glass was detected by the spectral analysis.

**[0025]** An inner part of the testpiece 3 was subjected to condensed irradiation with a peak energy density of 10<sup>8</sup>-10<sup>15</sup>W/cm<sup>2</sup> using a pulsed laser beam 1 of 1100nm wavelength with 120 femtoseconds pulse width and 200kHz a repetition rate. In Example 2, the testpiece 3 was shifted at a speed of 20μm/second with respect to an optic axis of the laser beam 1.

**[0026]** A fluorescent spectrum at each of a part irradiated with the pulsed laser beam and a non-irradiated part was measured by excitation with a light beam of 515nm wavelength using the same confocus optical system as that in Example 1. The measurement result proved that Sm ion changed its valence from 2+ to 3+ only at a locus of the focal point 3 of the pulsed laser beam. The similar ionic valence change was recognized when a fluoride glass containing one or more of Ce, Nd, Pr, Eu, Tb, Dy, Tm, Yb, Ti, Mn, Cr, V, Fe, Cu, Mo and Rn ions.

## Example 3

**[0027]** A testpiece 3 of 10mm in length, 10mm in width and 5mm in thickness was prepared from a single crystal having compositions of AlF<sub>3</sub>: SrF<sub>3</sub>: LiF=1:1:1 (a mol ratio) and containing 1mol% Ce<sup>3+</sup>, and polished at an optical level. A pulsed laser beam of 550nm wavelength with 120 femtoseconds pulse width and 200kHz a repetition rate was emitted to the testpiece 3 in the manner such that the pulsed laser beam 1 was condensed at a focal point 2 adjusted to an inner part of the testpiece 3 with a peak energy density of 10<sup>8</sup>-10<sup>15</sup>W/cm<sup>2</sup>. In Example 3, the testpiece 3 was shifted under such the irradiating condition at a speed of 20μm/second with respect to an optical axis of the laser beam 1.

**[0028]** A fluorescent spectrum at each of a part irradiated with the pulsed laser beam and a non-irradiated part was measured by excitation with a light beam of

300nm wavelength using the same confocus optical system as that in Example 1. The measurement result proved that Ce ion changed its valence from 3+ to 4+ along a locus of the focal point 2, while Ce ion kept its original valence 3+ at the other part except the locus of the focal point 3. The similar valence change of Ce ion from 3+ to 4+ was detected when other crystals containing halide, oxide and/or chalcogenide were irradiated with condensed pulsed laser beams in the same way.

## INDUSTRIAL APPLICATION

**[0029]** According to the present invention as above-mentioned, ionic valence is changed at a focal point and its vicinity in an inner part of an inorganic body containing rare earth or transition metal ion by irradiating the inorganic body with a pulsed laser beam in a manner such that the focal point of the pulsed laser beam is adjusted to the inner part of the inorganic body. The ionic valence change occurs only at the focal point and its vicinity while the other part keeps its original ionic valence. As a result the inorganic body is reformed to such the state that an ionic valence-changed domain is surrounded with the remaining part which keeps the original ion valence. The partial change of the ion valence differentiates optical properties such as absorption and fluorescence, resulting in selective change of the optical properties at a specified domain in the inner part of the inorganic body. The inorganic body processed in this way is useful as a functional device such as a memory device or a light-emitting device using the differentiated optical properties.

## Claims

1. A method of selectively reforming an inner part of an inorganic body, which comprises:  
emitting a pulsed laser beam of wavelength different from absorption wavelength of rare earth and/or transition metal ion to an inorganic body containing said rare earth and/or transition metal ion, and  
condensing said pulsed laser beam at a focal point in an inner part of said inorganic body,  
whereby said rare earth and/or transition metal ion changes its valence only at said focal point and its vicinity.
2. The method of selectively reforming an inner part of an inorganic body defined in Claim 1, wherein the inorganic body is a glass or crystal containing one or more of oxide, halide and chalcogenide.
3. The method of selectively reforming an inner part of an inorganic body defined in Claim 1 or 2, wherein the rare earth ion is one or more of Ce, Nd, Pr, Sm, Eu, Tb, Dy, Tm and Tb ions.

4. The method of selectively reforming an inner part of an inorganic body defined in Claim 1 or 2, wherein the transition metal ion is one or more of Ti, Mn, Cr, V, Fe, Cu, Mo and Ru ions.
5. The method of selectively reforming an inner part of an inorganic body defined in either one of Claims 1 to 5, wherein the focal point is relatively shifted with respect to the inorganic body so as to form a domain with a predetermined pattern where the rare earth and/or transition metal ion changes its valence.
6. The method of selectively reforming an inner part of an inorganic body defined in either one of Claims 1 to 6, wherein the inorganic body is irradiated with a pulsed laser beams with pulse width under a pico-second.
7. An inorganic body having such the selectively reformed inner part that a domain where valence of rare earth and/or transition metal ion is changed by condensed irradiation of a pulsed laser beam of wavelength different from absorption wavelength of said rare earth and/or transition metal ion is formed with a predetermined pattern in an inner part of said inorganic body.

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FIG. 1

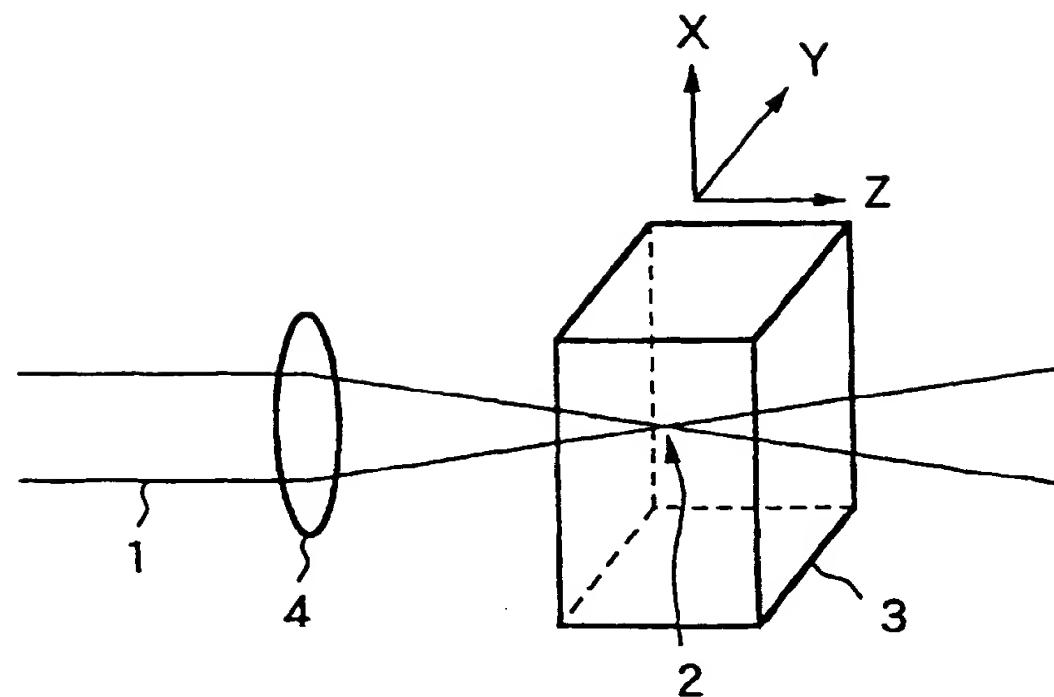


FIG. 2

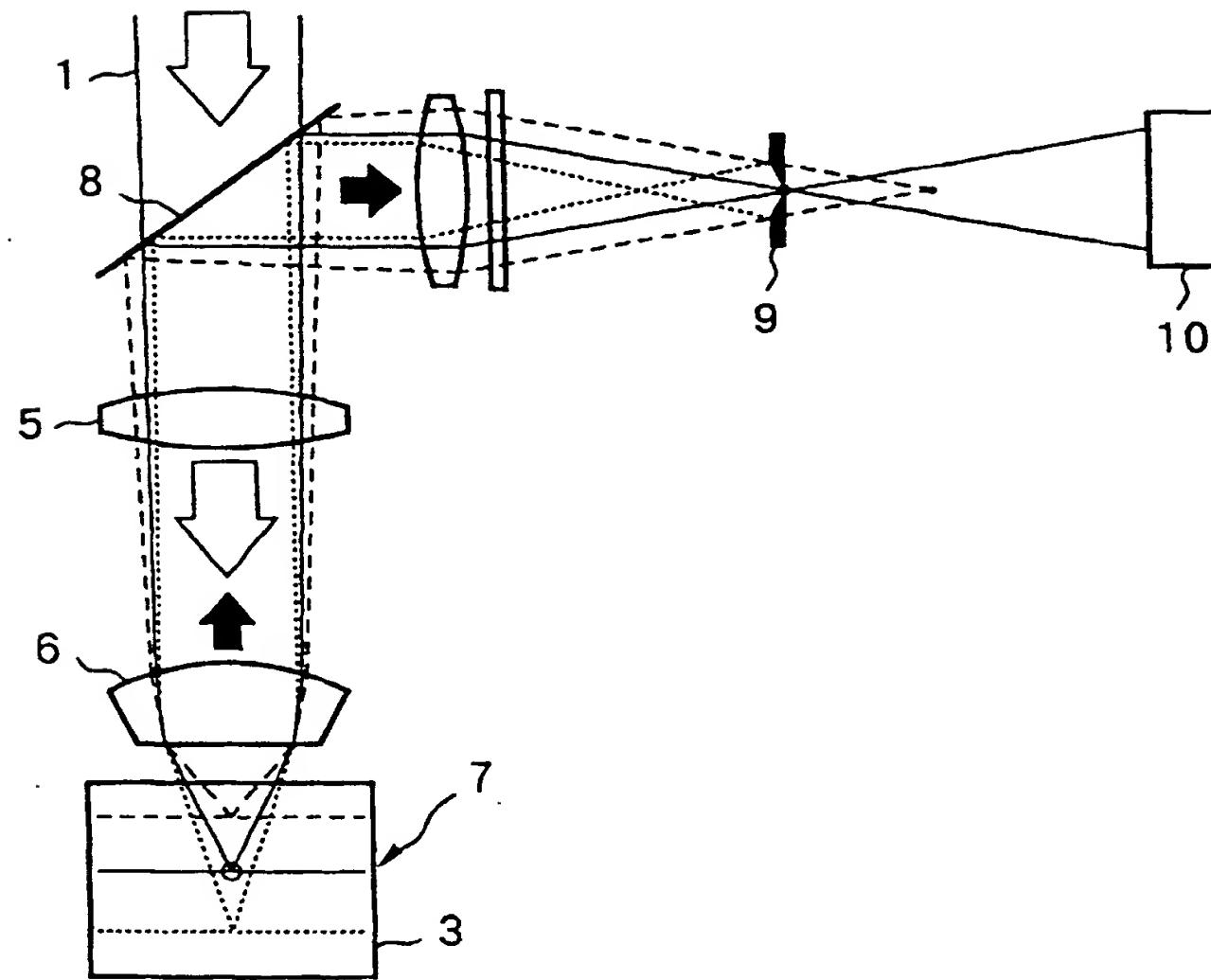
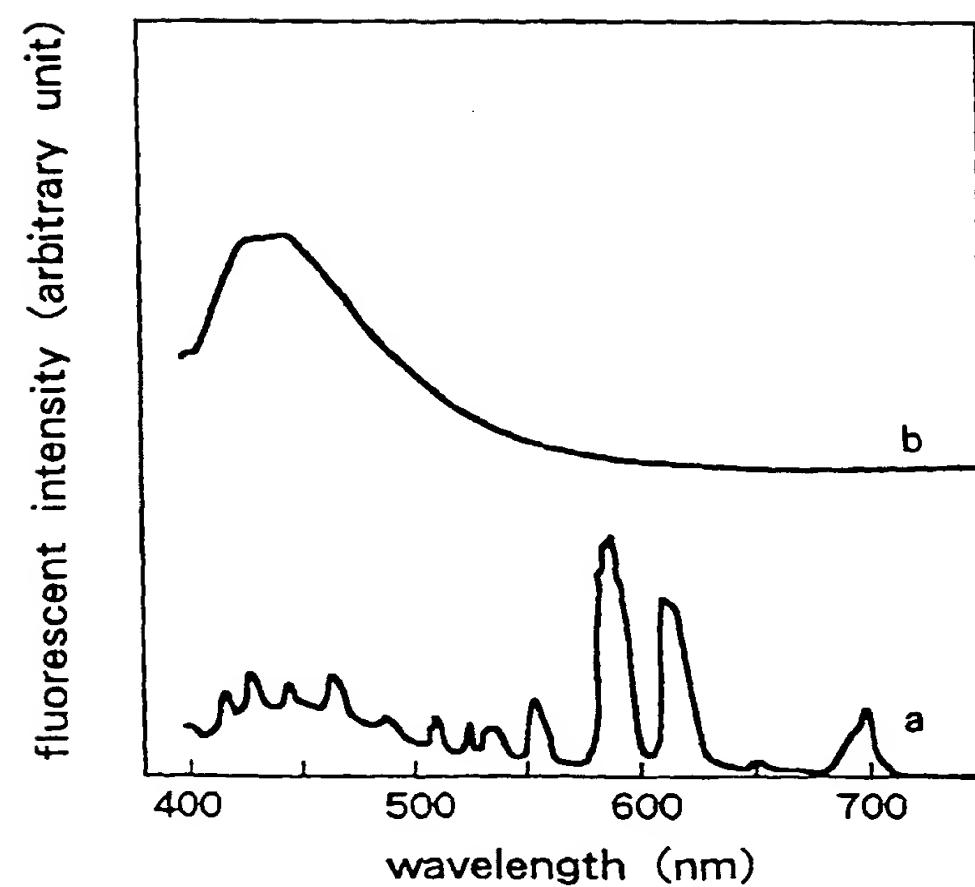


FIG.3



a : fluorescent spectrum of  $\text{Eu}^{3+}$  in a zone irradiated with  
a pulsed laser

b : fluorescent spectrum of  $\text{Eu}^{2+}$  in a non - irradiated zone

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05676

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl' B01J19/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
Int.Cl' B01J19/12, C30B33/00, H01L27/00Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Jitsuyo Shinan Koho 1926-1999 Toroku Jitsuyo Shinan Koho 1994-1999  
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Keisai Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 8-301695, A (Nippon Telegraph & Telephone Corp.), 19 November, 1996 (19. 11. 96), Claims ; Examples 1 to 5 (Family: none)	1-7
X	JP, 8-288582, A (Nippon Telegraph & Telephone Corp.), 1 November, 1996 (01. 11. 96), Claims (Family: none)	1-7
A	JP, 6-89999, A (Nippon Telegraph & Telephone Corp.), 29 March, 1994 (29. 03. 94), Claims ; Par. Nos. [0006] to [0009] (Family: none)	1-7
A	JP, 60-191024, A (Toshiba Corp.). 28 September, 1985 (28. 09. 85), Claims (Family: none)	1-7

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search  
16 March, 1999 (16. 03. 99)Date of mailing of the international search report  
30 March, 1999 (30. 03. 99)Name and mailing address of the ISA/  
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